Condensed Thiophen Ring Systems. Part XVIII.[1,2] Thienoazepines and Thienobenzoxazoles from 6-Azidobenzo[*b*]thiophens

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Photolysis of 6-azido-2,3-dibromobenzo[*b*]thiophen (11) in an excess of diethylamine for 18 h gave mainly 7-amino-2,3-dibromo-6-diethylaminobenzo[*b*]thiophen (13). After 9 h the major product was 2,3-dibromo-6-diethylamino-8*H*-thieno[2,3-*c*]azepine (15). In the presence of pyrene and with a reaction time of 18 h, 6-azidobenzo[*b*]thiophen (9), its 2,3-dibromo-derivative (11), and methyl 6-azidobenzo[*b*]thiophen-2-carboxylate (10) gave 7-amino-6-diethylaminobenzo[*b*]thiophen (14) and 6-aminobenzo[*b*]thiophen (no thienoazepine in this case), the thienoazepine (15), and methyl 6-diethylamino-8*H*-thieno[2,3-*c*]azepine-2-carboxylate (16), respectively. Thermolysis of the azides (10) and (11) in a mixture of polyphosphoric and acetic acids gave the corresponding 2-methylthieno[3,2-*g*]benzoazoles, (19) and (20) (angular products), respectively; 6-azidobenzo[*b*]thiophen 1,1-dioxide (12) gave the linear product, 2-methylthieno [2,3-*f*]benzoxazole 5,5-dioxide (21), under these conditions.

PREVIOUSLY we reported that photolysis of 4-azidobenzo[*b*]thiophen in diethylamine for 24 h gives 4-aminobenzo[*b*]thiophen and 4,4′-azobenzo[*b*]thiophen, and 5-azidobenzo[*b*]thiophen (1) and ethyl 5-azidobenzo[*b*]-thiophen-2-carboxylate (2) yield the corresponding 4-amino-5-diethylaminobenzo[*b*]thiophen (5).[3] We reported also that thermolysis of the 5-azidobenzo[*b*]thiophens (1)—(4) in a mixture of polyphosphoric and acetic acids gives the corresponding 2-methylthieno[2,3-*g*]-benzoxazole (6) (angular products), whereas 5-azidobenzo[*b*]thiophen 1,1-dioxide (7) gives the linear product, 2-methylthieno[3,2-*f*]benzoxazole 7,7-dioxide (8).[4]

We now report the synthesis and corresponding reactions of the 6-azidobenzo[*b*]thiophens (9)—(11) (see Scheme) and (12). These azides were prepared from the corresponding amines in the usual way.[4] We began our work with 6-azido-2,3-dibromobenzo[*b*]thiophen because 6-amino-2,3-dibromobenzo[*b*]thiophen [5] seemed to be the most accessible 6-aminobenzo[*b*]-thiophen.[6] 6-Aminobenzo[*b*]thiophen itself was not readily available at the time.[7] In 1972, however, Beck [8] reported a convenient synthesis of methyl 6-nitrobenzo[*b*]thiophen-2-carboxylate, which gave the corresponding amine on reduction. Successive hydrolysis and decarboxylation of the former gave 6-nitrobenzo[*b*]thiophen, which was reduced to 6-aminobenzo[*b*]thiophen. 6-Nitrobenzo[*b*]thiophen 1,1-dioxide, readily available by nitration of benzo[*b*]thiophen 1,1-dioxide,[9] was reduced to the corresponding amine 1,1-dioxide. All attempts to reduce the dioxide further to 6-aminobenzo[*b*]thiophen failed. For example, reduction with lithium aluminium hydride under con-

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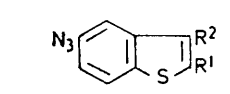
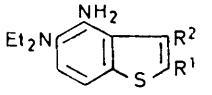
[2] Part XVII, B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Perkin I*, 1974, 2505.
[3] B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Perkin I*, 1974, 579; *J.C.S. Chem. Comm.*, 1972, 879.
[4] B. Iddon, H. Suschitzky, D. S. Taylor, and M. W. Pickering, *J.C.S. Perkin I*, 1974, 575.
[5] Y. Matsuki and T. Kanda, *Nippon Kagaku Zasshi*, 1965, **86**, 637 (*Chem. Abs.*, 1966, **65**, 674).
[6] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 287.
[7] C. Hansch, B. Schmidhalter, F. Reiter, and W. Saltonstall, *J. Org. Chem.*, 1956, **21**, 265; C. Hansch and B. Schmidhalter, *ibid.*, 1955, **20**, 1056.
[8] J. R. Beck, *J. Org. Chem.*, 1972, **37**, 3224.
[9] F. Challenger and P. H. Clapham, *J. Chem. Soc.*, 1948, 1615; D. E. Boswell, J. A. Brennan, P. S. Landis, and R. G. Rodewald, *J. Heterocyclic Chem.*, 1968, **5**, 69; W. Davies and Q. N. Porter, *J. Chem. Soc.*, 1957, 826; J. Bolssens, J. A. C. Th. Brouwers, J. H. Choufoer, A. Kats, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1954, **73**, 819.

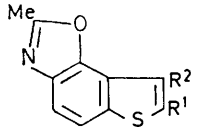
ditions which deoxygenate 3-(secondary amino)benzo[*b*]-thiophen 1,1-dioxides [10] gave only starting material as did use of Raney nickel and hydrogen, and treatment



(1) $R^1 = R^2 = H$
(2) $R^1 = CO_2Et$, $R^2 = H$
(3) $R^1 = CO_2Me$, $R^2 = H$
(4) $R^1 = H$, $R^2 = Me$



(5)



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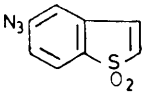

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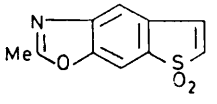

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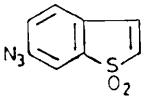


(12)

with triethyl phosphite gave an intractable product. An attempt to reduce 6-nitrobenzo[*b*]thiophen 1,1-dioxide with Raney nickel and hydrazine in ethanol also yielded an intractable product.

Photolysis (with a high-pressure mercury vapour lamp through a Pyrex filter) of 6-azido-2,3-dibromobenzo[*b*]-thiophen (11) (see Scheme) for 18 h in an excess of diethylamine under nitrogen gave 7-amino-2,3-dibromo-6-diethylaminobenzo[*b*]thiophen (13) (13% yield) together with a trace of 2,3-dibromo-6-diethylamino-8*H*-thieno[2,3-*c*]azepine (15). Irradiation for only 9 h gave a trace of the diamine (13) and the thienoazepine (15) (12%); addition of pyrene (a triplet quencher) to the reaction mixture and irradiation for 18 h gave the thienoazepine (15) as the only isolable product in a significantly increased yield (22%). In the same way methyl 6-azidobenzo[*b*]thiophen-2-carboxylate (10) gave methyl 6-diethylamino-8*H*-thieno[2,3-*c*]azepine-2-carboxylate (16) (34%). Surprisingly, however, photolysis of 6-azidobenzo[*b*]thiophen (9) in an excess of diethylamine for 18 h *in the presence of pyrene* gave only 7-amino-6-diethylaminobenzo[*b*]thiophen (14) (25%) and 6-aminobenzo[*b*]thiophen (9%), together with an intractable tar. So far, we have only been able to isolate products of ring expansion of 6-azidobenzo[*b*]thiophens. When a mixture of ethyl 5-azidobenzo[*b*]thiophen-2-carboxylate (2) and diethylamine was irradiated for 9 instead of 24 h (but in the absence of pyrene) it gave only the corresponding diamine (5), but in higher yield than before.[3]

Our results show striking differences amongst the reactions of 4-, 5-, and 6-azidobenzo[*b*]thiophens on irradiation in diethylamine. Furthermore, we appear to have discovered the first photolytically initiated ring expansions of condensed bicyclic aromatic azides to azepines. Previous attempts to expand such systems (*e.g.* azidonaphthalenes [11-13]) have proved abortive.

Compounds (15) and (16) are the first examples of 8*H*-thieno[2,3-*c*]azepines and are of interest also as members of the uncommon '2*H*-azepine' class. Since our earlier survey [3] of the limited literature on thienoazepines, Weiss *et al.*[14] have reduced the carbonyl group in 5,6,7,8-tetrahydrothieno[3,2-*c*]azepine-4-one and claim that *N*-substituted derivatives of the product exhibit antimicrobial activity.

A mechanism which accounts for the formation of the 8*H*-thieno[2,3-*c*]azepines (15) and (16) as well as the diamines (13) and (14) is shown in the Scheme. The increased yield of the thienoazepine (15) in the presence of pyrene suggests the intermediacy of singlet nitrenes in the formation of these compounds. The failure to isolate a thienoazepine from the product of photolysis of 6-azidobenzo[*b*]thiophen may be due to the absence of an electron-withdrawing substituent in the starting material. Such substituents may help to stabilise thienoazepines (15) and (16) (or a precursor) and thereby slow down collapse to diamines. A few azepines have been reported to collapse to diamines previously (see ref. 3). The apparent increased yield (<5% to 13%) of diamine (13) with increased reaction time (9 to 18 h) supports this suggestion; *i.e.* that the diamines are products of thermodynamic control whereas the thienoazepines are products of kinetic control (see ref. 15). The key intermediates, however, are probably the '1*H*-azepines' (Scheme) which may or may not be in equilibrium with the '2*H*-azepines' isolated. Irradiation of the thienoazepine (15) in an excess of diethylamine for 9 h was inconclusive and gave only tar. The alternative pathway shown in the Scheme to account for the formation of the diamines cannot be ruled out at the present time.

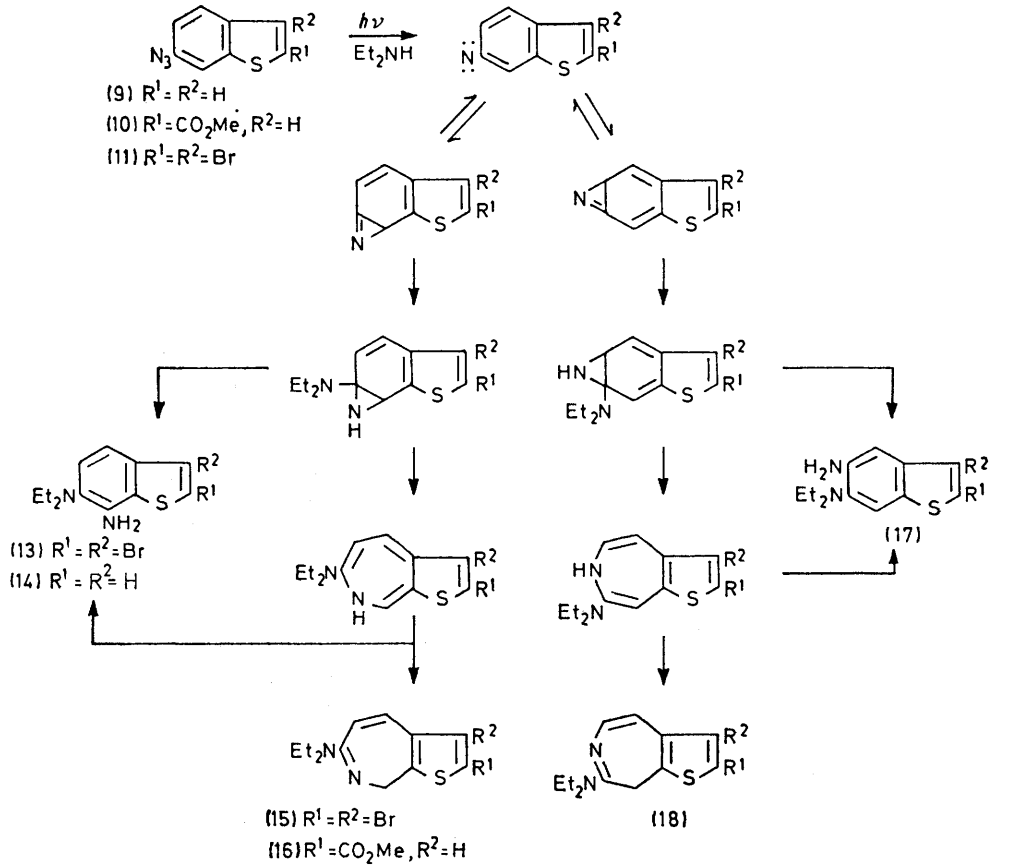
Equilibrium between the initially generated nitrenes and the alternative azirines would lead to the formation of diamines (17) together with thienoazepines (18), which may be regarded as members of the more common '3*H*-azepine' class. This equilibrium appears less favourable, however, than that already discussed because it results in a loss of aromaticity in both rings. Furthermore, fixation of a 6,7-double bond would be expected to favour attack at the 7-position over attack

[10] G. van Zyl, D. C. De Jongh, V. L. Heasley, and J. W. Van Dyke, *J. Org. Chem.*, 1961, **26**, 4946.
[11] R. Huisgen, D. Vossius, and M. Appl, *Chem. Ber.*, 1958, **91**, 1; R. Huisgen and M. Appl, *ibid.*, p. 12.
[12] R. Selvarajan and J. H. Boyer, *J. Org. Chem.*, 1971, **36**, 3464.
[13] S. E. Hilton, E. F. V. Scriven, and H. Suschitzky, *J.C.S. Chem. Comm.*, 1974, 853.
[14] M. J. Weiss, G. J. Gibs, J. F. Poletto, and W. A. Remers, U.S.P. 3,758,501/1973 (*Chem. Abs.*, 1973, **79**, 11,550).
[15] R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Amer. Chem. Soc.*, 1972, **94**, 1374.

at the 5-position. The change of product ratio with change of conditions in our experiments suggests that the isolated diamines and thienoazepines are derived from a common intermediate. The assignments of the structures of our diamines,(13) and (14), are unequivocal (n.m.r.), which suggests that our thienoazepines possess structures (15) and (16). If they had structures (18; $R^1 = R^2 = Br$ or $R^1 = CO_2Me$, $R^2 = H$), then one would expect their formation to be accompanied by the formation of diamines (17), none of which were detected.

atoms (probably predominantly with the former) as evidenced by a shift of the $CH_3{\cdot}CH_2$ signal. The singlet (originally at τ 5.80) for the ring methylene protons was considerably shifted downfield by addition of $Eu(fod)_3$ while the olefinic proton signals were shifted no more than those of the exocyclic methylene protons.

Thermolysis of methyl 6-azidobenzo[*b*]thiophen-2-carboxylate (10) and 6-azido-2,3-dibromobenzo[*b*]thiophen (11) in a mixture of polyphosphoric and acetic acids gave the corresponding thieno[3,2-*g*]benzoxazoles



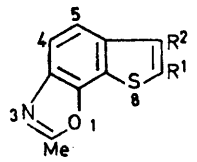
SCHEME

Doering and Odum [16] reported that a methylene group adjacent to an amidine carbon atom resonates at higher field (τ 7.47—7.62) than one next to an amidine nitrogen atom (τ 6.74—6.80). The chemical shifts (τ 5.80 and 5.78) of the methylene protons in our azepines, (15) and (16), respectively, are consistent with the structures assigned. The extra deshielding may be due to the electron-withdrawing character of the adjacent thiophen ring. Further support for these assignments was provided by a study of the effect of adding increasing amounts of the shift reagent $Eu(fod)_3$ on the spectrum of the dibromothienoazepine (15).* The shift reagent complexed between the ring and exocyclic nitrogen (19) and (20) (*i.e.* angular products), respectively whereas 6-azidobenzo[*b*]thiophen 1,1-dioxide (12) gave the linear product, 2-methylthieno[2,3-*f*]benzoxazole 5,5-dioxide (21). This contrasting behaviour parallels the results obtained with the 5-azidobenzo[*b*]thiophens (1)—(4) and the 1,1-dioxide (7) (mentioned before) and a similar explanation [4] can be given. Attempted oxazole formation from 6-azidobenzo[*b*]thiophen (9) gave no organic product. We concluded previously [4] that the reaction is promoted by an electron-withdrawing substituent in the thiophen ring of a 5-azidobenzo[*b*]thiophen and the present results with 6-azidobenzo[*b*]thiophens support this conclusion.

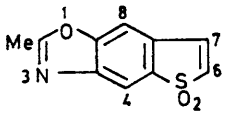
* We thank Dr. Gurnos Jones, University of Keele, for suggesting this experiment.

[16] W. von E. Doering and R. A. Odum, *Tetrahedron*, 1966, **22**, 81.

The identification of compounds (19)—(21) is based on elemental and spectroscopic analyses. The n.m.r. spectrum of the dibromo-compound (20) in a variety of solvents at 60 MHz consisted of two singlets only, one at τ 2.22 for the two aromatic protons, and one corresponding to the methyl group at τ 7.28. An attempt



(19) $R^1 = CO_2Me$, $R^2 = H$
(20) $R^1 = R^2 = Br$



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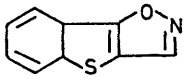

(22)

to separate the aromatic proton signals by formation of the methiodide of compound (20) was not completely successful. However, addition of $Eu(fod)_3$ to a solution of the parent compound (20) in chloroform separated these signals and showed that they constituted an AB system with J 9.0 Hz, in agreement with the proposed angular structure. The n.m.r. spectra of compounds (19) and (21) were unequivocal in the absence of a shift reagent.

Since our earlier report [4] on systems with an oxazole or isoxazole ring fused to a benzo[*b*]thiophen ring, Oikawa *et al.*[17] have reported a synthesis of 2-methylthieno[2,3-*f*]benzoxazole [*i.e.* the deoxygenated derivative of compound (21)], and Sauter and Büyük [18] have described several derivatives of the [1]benzothieno-[2,3-*d*]isoxazole (22) system.

EXPERIMENTAL

General comments (instruments used, *etc.*) are given previously.[4] Light petroleum refers to the fraction b.p. 60—80° unless stated otherwise. Calculated M values for mass spectra are for the ions containing ^{79}Br.*

Acetylation of 2,3-*Dibromobenzo*[b]*thiophen*.—2,3-Dibromobenzo[*b*]thiophen [19] (648.2 g, 2.22 mol) was dissolved in nitrobenzene (2.04 l) containing anhydrous aluminium chloride (326 g, 2.44 mol) at 0 °C and acetyl chloride (192 g, 2.44 mol) was added dropwise to the vigorously stirred slurry while the temperature was maintained at 0 °C. The mixture was then stirred for a further 8 h at 0 °C and poured into water (2 l) and 2M-hydrochloric acid (1 l). The product obtained from the organic layer was poured into light petroleum (2.5 l) and the precipitate (259.5 g, 35%) was filtered off and recrystallised several times from light petroleum (b.p. 80—100°) to give 6-acetyl-2,3-dibromobenzo[*b*]thiophen (177 g, 24%), m.p. 131—132° (lit.,[5] 132°). The n.m.r. spectrum of the crude product in chloroform showed that it was a mixture of the 4- and 6-acetyl isomers (29 : 71). Consequently, the mother liquors from the crystallisations were combined, the solvent was distilled off, and a sample (8 g) of the product was chromatographed on silica. Light petroleum–chloroform (4 : 1) eluted 4-*acetyl*-2,3-*dibromobenzo*[b]*thiophen* (7.0 g), m.p. 133—134° (from methanol), $\nu_{max.}$ (Nujol) 1 675 cm^{-1} (C:O); *m/e* 332 (M^+) (Found: C, 35.5; H, 1.7. $C_{10}H_6Br_2OS$ requires C, 35.9; H, 1.8%); followed by 6-acetyl-2,3-dibromobenzo[*b*]thiophen (0.5 g), identical with the sample isolated as described above.

The oxime, m.p. 224—225° (crude), of the 6-acetyl isomer was prepared in the usual way and used without purification as described in the next experiment.

6-*Acetamido*-2,3-*dibromobenzo*[b]*thiophen*.— Phosphorus pentachloride was added in four portions (6.3 g, 30 mmol each) to a stirred mixture of 6-acetyl-2,3-dibromobenzo-[*b*]thiophen oxime (20.1 g, 57.6 mmol) and ether (325 ml) at 0 °C, and the resultant solution was stirred at 0 °C for 3 h. Then it was allowed to warm to ambient temperature and was stirred at this temperature for a further 12 h. The mixture was poured into 4M-sodium hydrogen carbonate (1 l) and the precipitate was filtered off and washed well with water, to give 6-acetamido-2,3-dibromobenzo[*b*]thiophen (19.6 g, 98%), m.p. 202—204° (from ethanol) (lit.,[5] 200—201.5°). This compound was prepared also, in a slightly lower yield, by the procedure of Matsuki and Kanda [5] and was hydrolysed to 6-amino-2,3-dibromobenzo[*b*]thiophen by the procedure described by these authors.

6-*Nitrobenzo*[b]*thiophen*-2-*carboxylic Acid*.—This was prepared (85%) by hydrolysis with sodium hydroxide in aqueous ethanol of methyl 6-nitrobenzo[*b*]thiophen-2-carboxylate.[8] It had m.p. 305—307° (from acetic acid) [lit.,[20] 292—294° (decomp.)], $\nu_{max.}$ (Nujol) 3 200—2 450br (OH) and 1 680 cm^{-1} (C:O); *m/e* 179 ($M^+ - CO_2$; inlet temp. 150 °C) (Found: C, 48.2; H, 2.6; N, 5.8. $C_9H_5NO_4S$ requires C, 48.4; H, 2.3; N, 6.3%).

6-*Nitrobenzo*[b]*thiophen*.—Decarboxylation of the acid prepared as described in the preceding experiment with copper bronze and quinoline at 185 °C for 35 min and work-up in the usual manner gave 6-nitrobenzo[*b*]thiophen (67%), m.p. 82—82.5° (from light petroleum) (lit.,[21] 79—80°).

6-*Aminobenzo*[b]*thiophen*.—The amine, m.p. 115—116° (from aqueous ethanol) (lit.,[7] 114—115°), was prepared (89%) by reduction of 6-nitrobenzo[*b*]thiophen with iron and ammonium chloride (reaction time 3.5 h) by using the procedure described previously,[4] as well as by the method of Hansch *et al.*[7]

The following compounds were prepared similarly (reaction time given in parentheses after the % yield): 6-aminobenzo[*b*]thiophen 1,1-dioxide (83%) (4 h), m.p. 167—169° (from aqueous ethanol) (lit.,[22] 162—165°); *methyl* 6-*aminobenzo*[b]*thiophen*-2-*carboxylate* (70%) (2.5 h), m.p. 109—111° (from ethanol), $\nu_{max.}$ (Nujol) 3 460 and

* N.m.r. data are available as Supplementary Publication No. SUP 21416 (5 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

[17] Y. Oikawa, O. Setoyama, and O. Yonemitsu, *Heterocycles*, 1974, **2**, 21 (*Chem. Abs.*, 1974, **80**, 120 684).
[18] F. Sauter and G. Büyük, *Monatsh.*, 1974, **105**, 254.
[19] W. Ried and H. Bender, *Chem. Ber.*, 1955, **88**, 34.
[20] V. P. Mamaev and O. P. Shkurko, *Izvest. sibirsk., Otdel. Akad. Nauk S.S.S.R., Ser. khim. Nauk*, 1967, 122 (*Chem. Abs.*, 1968, **69**, 106 388).
[21] K. J. Armstrong, M. Martin-Smith, N. M. D. Brown, G. C. Brophy, and S. Sternhell, *J. Chem. Soc.* (*C*), 1969, 1766.
[22] F. Sauter, *Monatsh.*, 1968, **99**, 1591.

3 360 (NH_2) and 1 685 cm^{-1} (C:O) (Found: M^+, 207.0341. $C_{10}H_9NO_2S$ requires M, 207.0354).

6-*Azidobenzo*[b]*thiophen* (9).—This *azide*, m.p. 55—56° (from aqueous methanol), decomp. 118—120°, $\nu_{max.}$ (Nujol) 2 105 cm^{-1} (N_3); *m/e* 175 (M^+) (Found: C, 54.6; H, 2.8; N, 23.95. $C_8H_5N_3S$ requires C, 54.8; H, 2.9; N, 24.0%), was prepared (50%) by the procedure reported previously [4] for the synthesis of 5-azidobenzo[*b*]thiophens. The following compounds were prepared similarly: 6-*azidobenzo*[b]*thiophen* 1,1-*dioxide* (12) (62%), decomp. 165° (recrystallised from acetic acid), $\nu_{max.}$ (Nujol) 2 105 cm^{-1} (N_3) (Found: C, 46.2; H, 2.6; N, 19.9. $C_8H_5N_3O_2S$ requires C, 46.4; H, 2.4; N, 20.3%); *methyl* 6-*azidobenzo*[b]*thiophen*-2-*carboxylate* (10) (62%), m.p. 109—110° (from methanol), $\nu_{max.}$ (Nujol) 2 100 and 2 130 cm^{-1} (N_3) and 1 710 cm^{-1} (C:O); *m/e* 233 (M^+) (Found: C, 51.6; H, 3.1; N, 17.6. $C_{10}H_7N_3O_2S$ requires C, 51.5; H, 3.0; N, 18.0%); and 6-*azido*-2,3-*dibromobenzo*[b]*thiophen* (11) (60%), m.p. 118—119° (from ethanol), $\nu_{max.}$ (Nujol) 2 150 and 2 130 cm^{-1} (N_3); *m/e* 331 (M^+) (Found: C, 29.0; H, 1.3; N, 12.3. $C_8H_3Br_2N_3S$ requires C, 28.85; H, 0.9; N, 12.6%).

Photolysis of 6-*Azido*-2,3-*dibromobenzo*[b]*thiophen* (11).—(*a*) A solution of the azide (11) (1.0 g, 3.0 mmol) in diethylamine (70 ml) was irradiated under nitrogen with a high-pressure mercury vapour lamp through a Pyrex filter for 18 h. The excess of diethylamine was distilled off under reduced pressure and the product was chromatographed on alumina. Light petroleum–chloroform (70 : 30) eluted 7-*amino*-2,3-*dibromo*-6-*diethylaminobenzo*[b]*thiophen* (13) (0.15 g, 13%), b.p. 148—150° at 3.0 mmHg, $\nu_{max.}$ (film) 3 450 and 3 350 cm^{-1} (NH_2); *m/e* 376 (M^+) (Found: C, 38.4; H, 3.3. $C_{12}H_{14}Br_2N_2S$ requires C, 38.1; H, 3.7%); and a trace (<5%) of 2,3-dibromo-6-diethylamino-8*H*-thieno[2,3-*c*]azepine (15), identical (m.p. and i.r. and n.m.r. spectra) with the samples prepared as described in (*b*) and (*c*).

(*b*) When the experiment described in (*a*) was repeated with a reaction time of only 9 h, work-up in the manner described in (*a*) gave a trace (<5%) of 7-amino-2,3-dibromo-6-diethylaminobenzo[*b*]thiophen (13) and 2,3-*dibromo*-6-*diethylamino*-8H-*thieno*[2,3-c]*azepine* (15) (12%), m.p. 110—112° (from light petroleum), $\nu_{max.}$ (Nujol) 1 630 cm^{-1} (C:N) (Found: C, 38.5; H, 3.3; N, 7.4%; M^+, 375.9235. $C_{12}H_{14}Br_2N_2S$ requires C, 38.1; H, 3.7; N, 7.4%; M, 375.9243).

(*c*) A reaction carried out for 18 h and worked up as described in (*a*) but with pyrene [6.06 g, 30.0 mmol, to 15.0 mmol of the azide (11) in 1 l of diethylamine] added gave only the thienoazepine (15) (1.25 g, 22%), identical (m.p. and i.r. and n.m.r. spectra) with the other samples.

Methyl 6-*Diethylamino*-8H-*thieno*[2,3-c]*azepine*-2-*carboxylate* (16).—*Compound* (16) (2.0 g, 34%), m.p. 66—68° (from light petroleum), $\nu_{max.}$ 1 710 (C:O) and 1 630 cm^{-1} (C:N), *m/e* 278 (M^+); *tartrate*, m.p. 209—210° (with decomp.) (prepared in aqueous ethanol and washed well with propan-2-ol), $\nu_{max.}$ (Nujol) 1 710 cm^{-1} (C:O) (Found: C, 50.0; H, 5.6; N, 6.3. $C_{18}H_{24}N_2O_8S$ requires C, 50.45; H, 5.65; N, 6.5%), was prepared similarly from methyl 6-azidobenzo[*b*]thiophen-2-carboxylate (10) (5.0 g, 21.3 mmol) and diethylamine (1 l) in the presence of pyrene (42.6 mmol) (reaction time 18 h).

Similar treatment of 6-azidobenzo[*b*]thiophen (9) (1.3 g, 7.4 mmol) gave only 7-*amino*-6-*diethylaminobenzo*[b]*thiophen* (14) (0.4 g, 25%), b.p. 175—177° at 0.7 mmHg, $\nu_{max.}$ (film) 3 460 and 3 360 cm^{-1} (NH_2) (Found: M^+, 220.1034. $C_{12}H_{16}N_2S$ requires M, 220.1034); and 6-aminobenzo[*b*]-thiophen (0.1 g, 9%), identical (m.p. and i.r. spectrum) with an authentic sample.

2-*Methyl*-6,7-*dibromothieno*[3,2-g]*benzoxazole* (20).—A vigorously stirred mixture of 6-azido-2,3-dibromobenzo[*b*]-thiophen (11) (0.5 g, 1.5 mmol), polyphosphoric acid (25 g), and acetic acid was heated to 130 °C during 30 min and was kept at this temperature for 10 min. Then it was cooled and poured into water (100 ml). The product was extracted with chloroform, the combined extracts were washed successively with 2M-sodium carbonate and water, and distillation left 2-*methyl*-6,7-*dibromo*[3,2-g]*benzoxazole* (20) (0.3 g, 57%), m.p. 162—164° (from ethanol), $\nu_{max.}$ (Nujol) 1 605 cm^{-1} (C:N) (Found: C, 34.5; H, 1.4; N, 3.9%; M^+, 344.8467. $C_{10}H_5Br_2NOS$ requires C, 34.6; H, 1.45; N, 4.0%; M, 344.8459); methiodide, m.p. 250° (with decomp.) (from aqueous ethanol).

Methyl 2-*methylthieno*[3,2-g]*benzoxazole*-7-*carboxylate* (19) (57%), m.p. 167—168° (from light petroleum–carbon tetrachloride), $\nu_{max.}$ (Nujol) 1 710 (C:O) and 1 605 cm^{-1} (C:N); *m/e* 247 (M^+) (Found: C, 55.6; H, 3.5; N, 5.7%; M^+, 247.0296. $C_{12}H_9NO_3S \cdot 0.75H_2O$ requires C, 55.3; H, 4.1; N, 5.4%; M, 247.0303); and 2-*methylthieno*[2,3-f]*benzoxazole* 5,5-*dioxide* (21) (36%), m.p. 236—238° (sublimed, 166—170° at 2.0 mmHg) (Found: C, 53.8; H, 3.3; N, 6.1. $C_{10}H_7NO_3S$ requires C, 54.3; H, 3.2; N, 6.3%), were prepared similarly. In the former case the reaction mixture was kept at 150 °C for 1 h; in the latter the corresponding figures were 135 °C for 2 h.

When 6-azidobenzo[*b*]thiophen (9) was treated similarly, even at 70 °C for 5 min, no organic product was isolated on work-up.

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